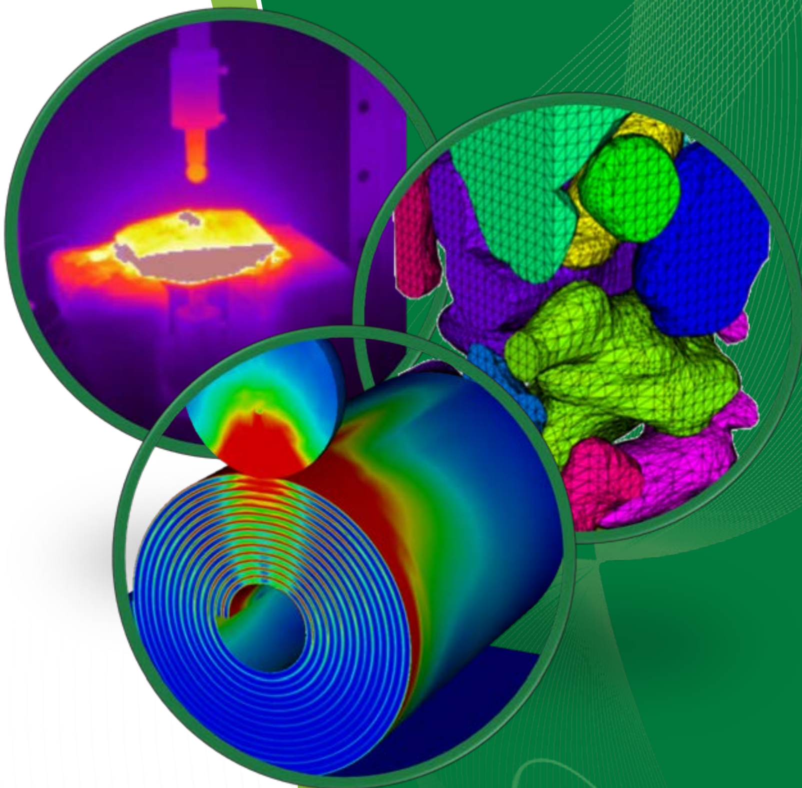
Exploring How Electrode Structure Affects Electrode-Scale Properties Using 3-D Mesoscale Simulations



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Organization: Sandia National Laboratories

Team: Consortium for Advanced Battery Simulation

2017 U.S. DOE Vehicle Technologies Office Annual Merit Review

June 6, 2017 **Project ID:** ES303

CABS Consortium for Advanced Battery Simulation

Oak Ridge National Laboratory | Argonne National Laboratory | Berkeley Lab | Sandia National Laboratories

Overview

Timeline

- Project Start Date: Oct 1, 2015
- Project End Date: Sept 30, 2018
- Percent Complete: 55%

Barriers Addressed

- **Life:** Loss of available power and energy due to use and aging, and the lack of accurate life prediction capability.
- **Abuse Tolerance, Reliability and Ruggedness:** It is critical that any new technology introduced into a vehicle be abuse tolerant under both routine and extreme operating conditions.

Budget

- FY16
  - Total CABS: $2,265k
  - SNL Effort: $550k
- FY17
  - Total CABS: $2,225k
  - SNL Effort: $500k

Partners

- Project Partners/Consortium:
  - Oak Ridge National Laboratory
  - Lawrence Berkeley National Laboratory
- NREL-led CAEBAT team
  - SNL, TAMU

Relevance / Objectives

- Project Objectives
  - Improve the fidelity of battery-scale simulations of abuse scenarios through the creation and application of microscale (particle-scale) electrode simulations
- Present Year Objectives
  - Accurately represent NMC microstructure, including the active binder phase, within the simulation framework
  - Begin to feed information from the microscale to the battery scale
- Impact to VTO
  - Improve ability to assess battery response to abuse scenarios (e.g. crush) computationally, enabling many parametric computer tests rather than expensive and dangerous experiments

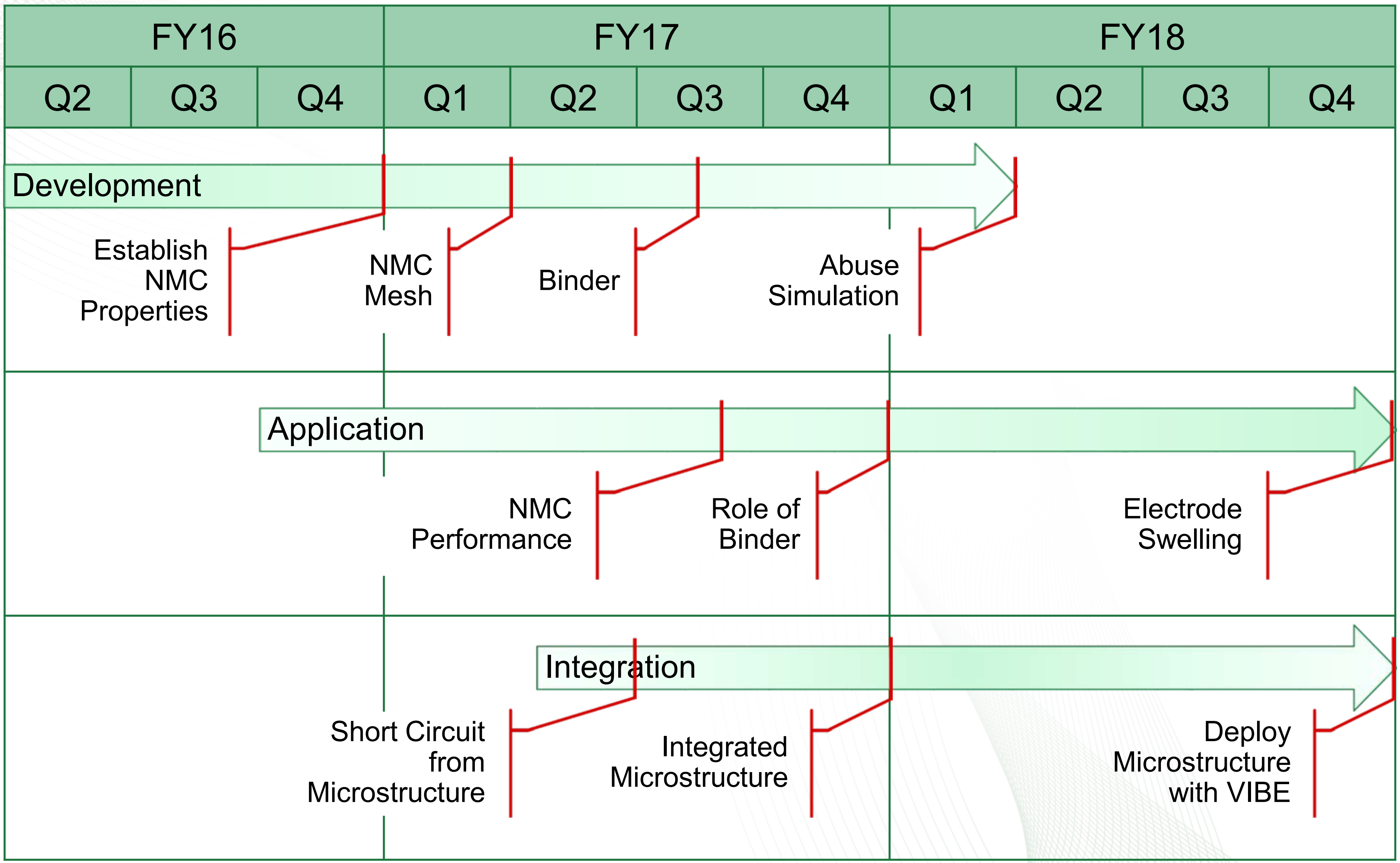
CABS Milestones (FY16)

IDs indicate whether milestones are primarily experimental (E), computational (C), or integrated (I).							
ID	FY16	Lead	Q1	Q2	Q3	Q4	Status
C.1	Baseline performance profile of VIBE/OAS/AMPERES	ORNL	P				Complete
I.1	Report on experimental techniques supporting models	ORNL		P			Complete
E.1	Produce segmented tomographic reconstructions of electrodes for conversion to spatial domains for microstructural models	LBNL			P		Complete
E.2	Demonstration of single side indentation test with incremental deformation to determine faulting in spirally wound, wound prismatic, and stacked electrodes in hard case	ORNL				P	Complete
C1.1	***Collect constitutive models for NMC materials and report on use of mesoscale data to project lead.***	***SNL***				***P***	***Complete***
I.2	Deployment of VIBE/OAS with enhanced extensibility and hybrid models	ORNL				S	Complete

CABS Milestones (FY17)

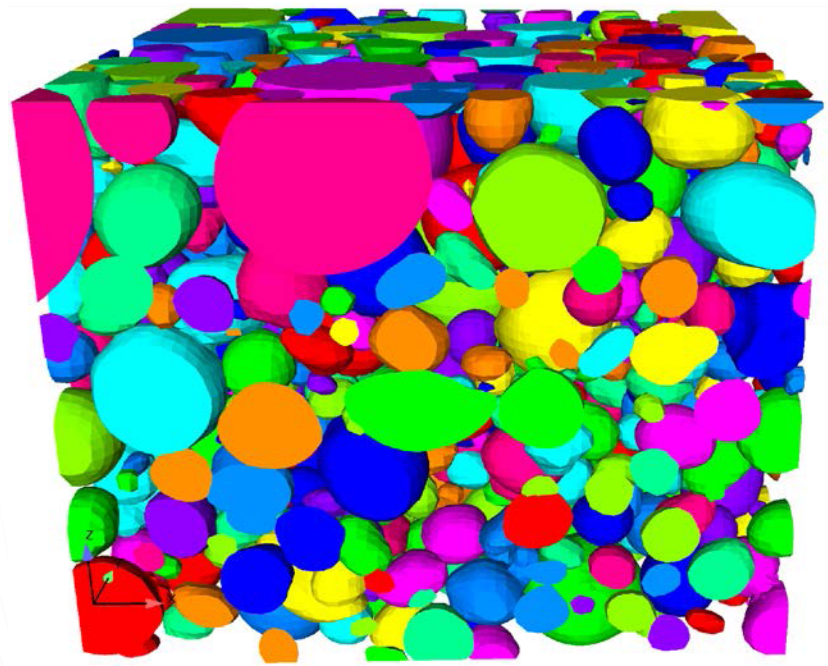
IDs indicate whether milestones are primarily experimental (E), computational (C), or integrated (I).							
ID	FY17	Lead	Q1	Q2	Q3	Q4	Status
I.3	***Demonstration of ability to construct 3D meshes of electrodes using reconstructions from micro-tomography***	***SNL***	***P***				***Complete***
E.3	Potential-dependent solid diffusivities for Li-ion and EIS	LBNL		P			Complete
I.4	*Demonstrated ability of VIBE/OAS to simulate onset of short-circuit due to mechanical abuse informed by microstructure*	*ORNL*		*D*			*Complete*
E.4	Data from mechanical deformation tests	ORNL			P		Ongoing
C.2	Validated constitutive models and failure criteria for electrode materials and spirally wound, wound prismatic, and stacked electrodes under indentation	ORNL				P	Ongoing
I.5	*Deployment of VIBE/OAS with integrated multiscale capability*	*ORNL*				S	*Ongoing*

Approach / Milestones



Technical: NMC Microstructure – Data

- Synchrotron X-ray tomography data from ETH-Zurich
  - 16 distinct data sets (0-2000 bar, 90-96 wt%)
  - 370 nm resolution
  - > 10,000 particles per set
  - 11 μm mean particle diameter

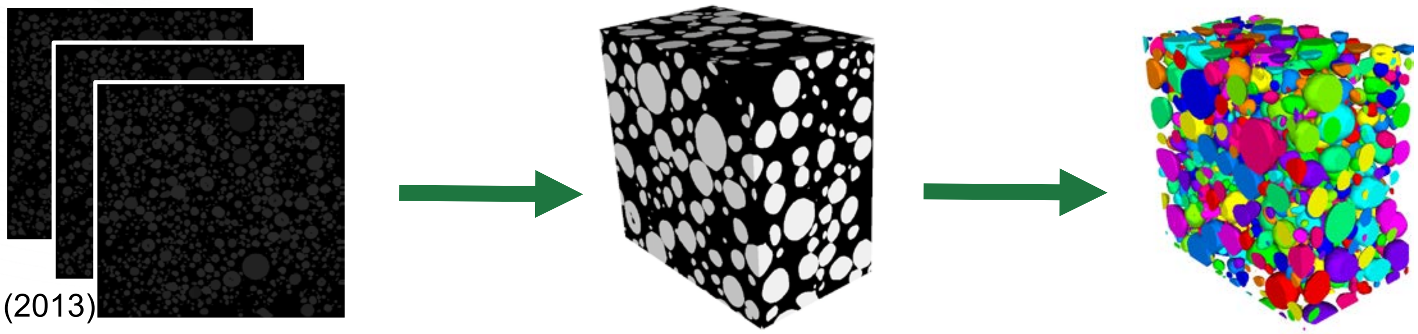


Roberts (2014), Ebner (2013)

High-quality image data available in literature

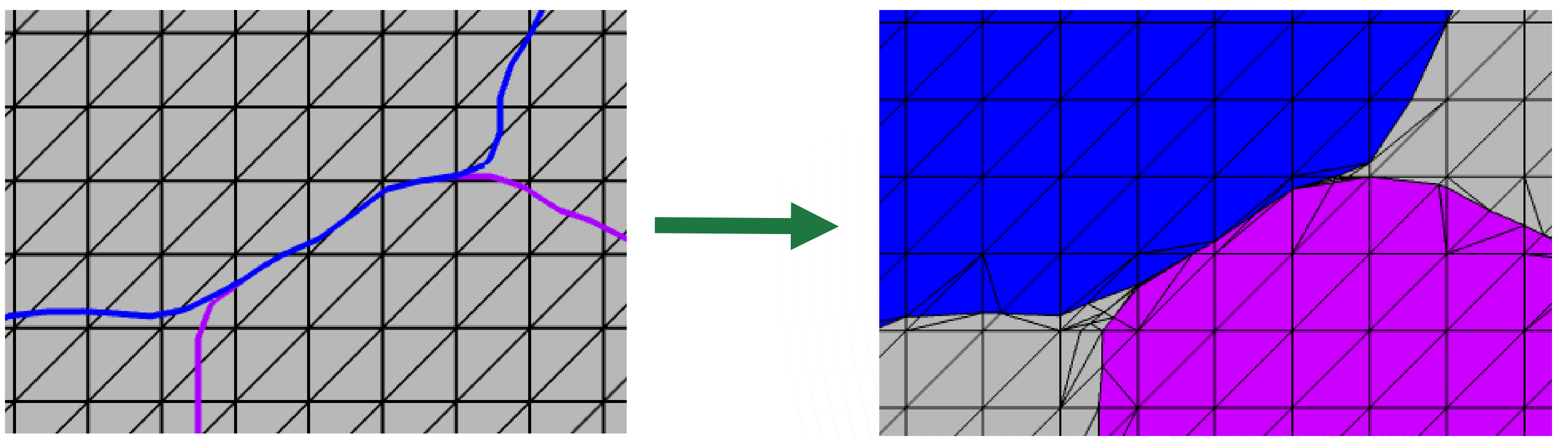
Technical: NMC Microstructure – CDFEM

- Conformal Decomposition Finite Element Method (CDFEM)
  - Individual cathode particle STL files processed and imported



Ebner (2013)

  - Background mesh sliced/decomposed using level-set fields

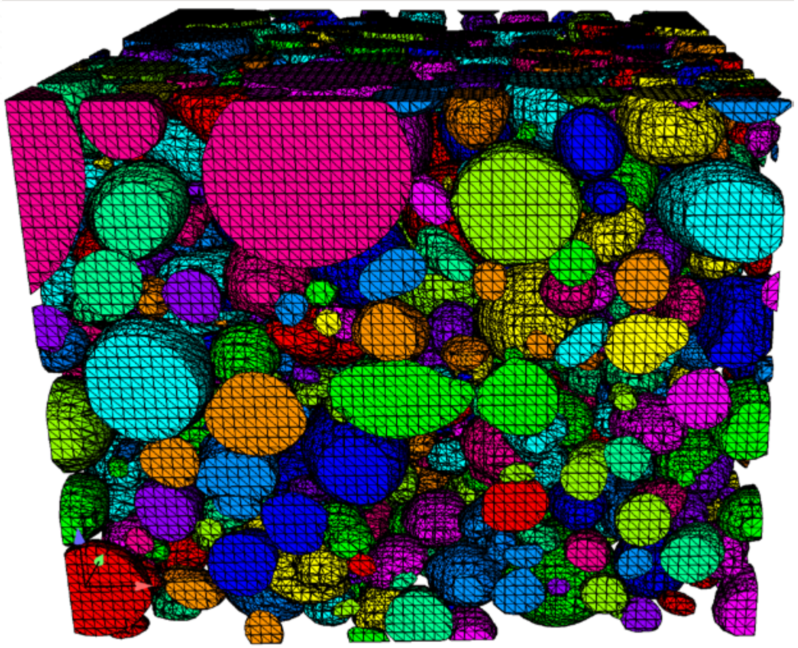


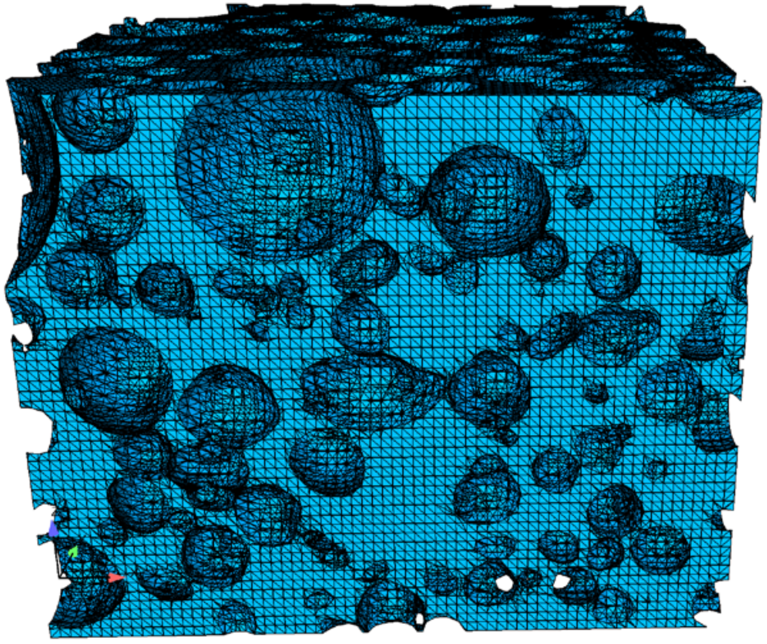
Roberts (2014)

CDFEM enables rapid meshing of experimental data

Technical: NMC Microstructure – Result

- Conformal meshes of both particle and electrolyte phases

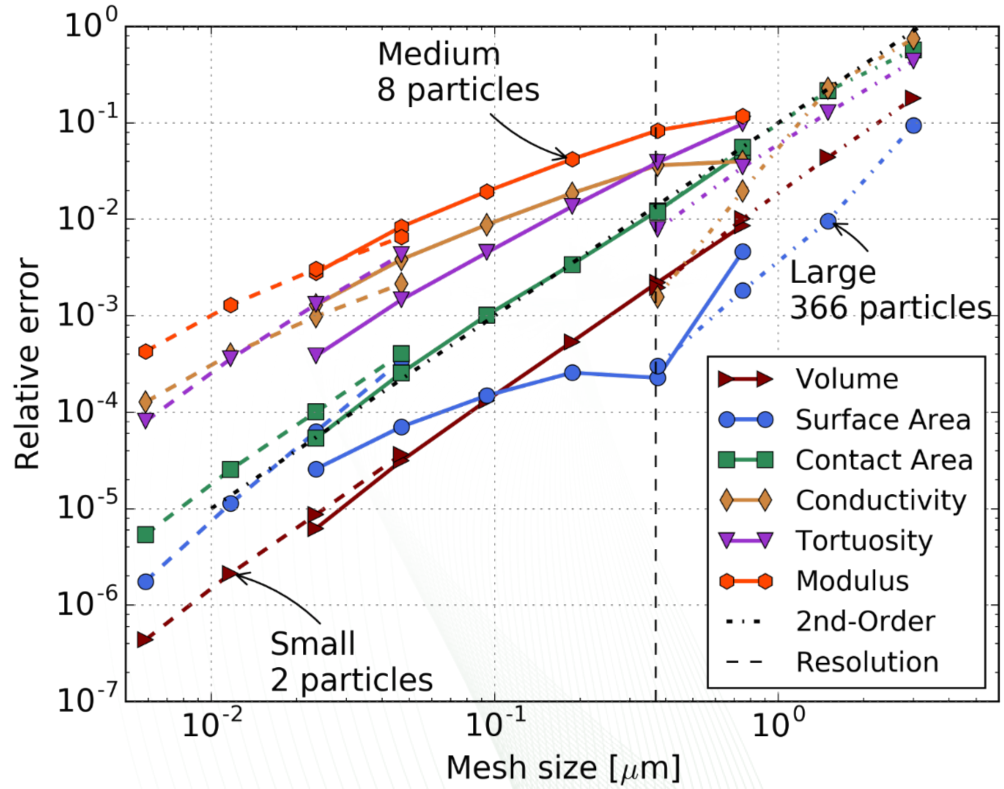




Quickly create large, high-quality microstructure meshes

Technical: Solution Verification – Convergence

- Solution verification of NMC microstructure shows
  - Ideal order-of-convergence
    - 2nd order for all QOIs
  - Required mesh resolution
    - Geometry converges quickly
    - Physics converge more slowly
    - Recommend simulating at image resolution (~0.35 μm)

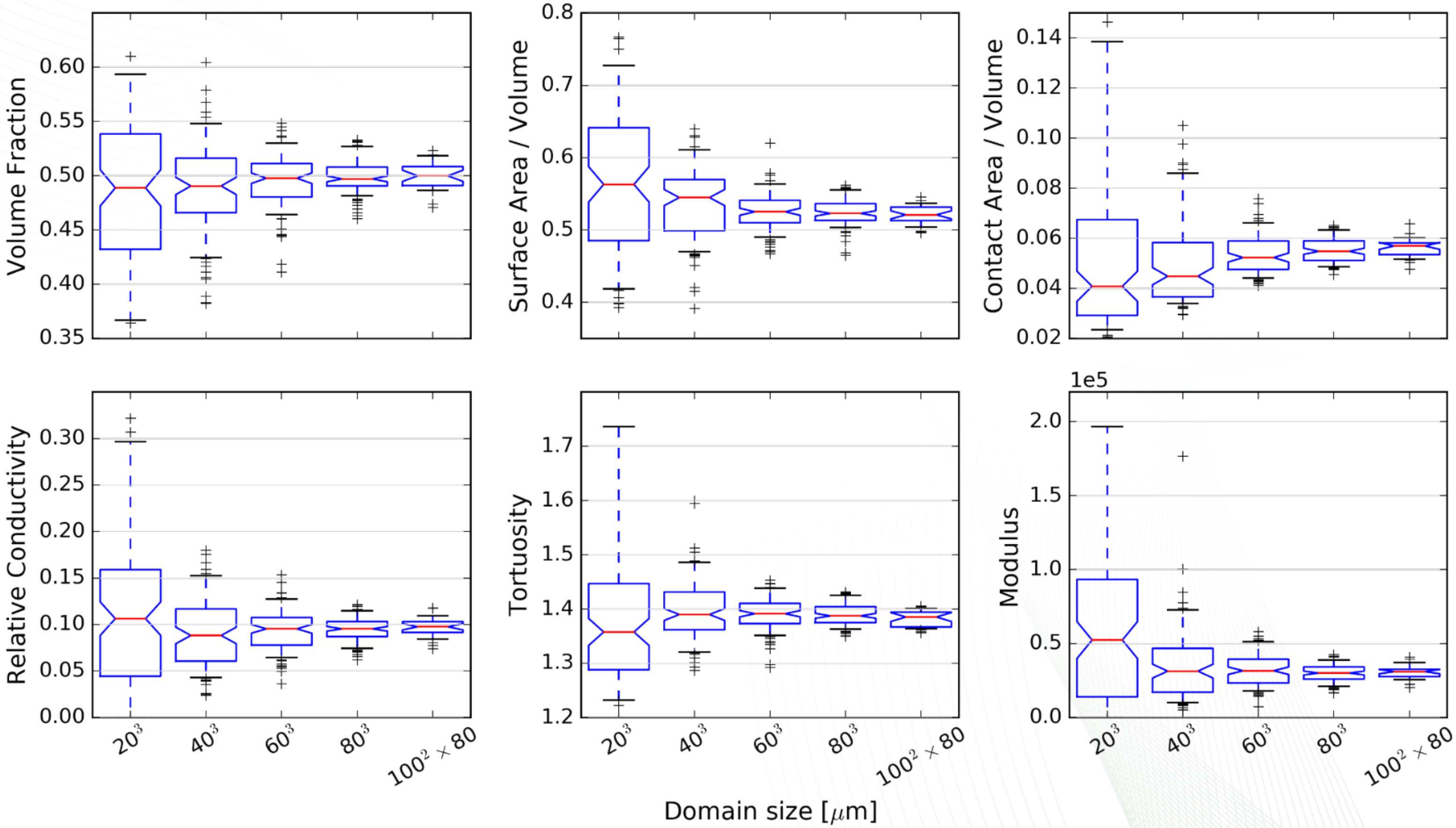


Roberts (submitted)

CDFEM convergent on NMC microstructure

Technical: Solution verification – domain

- How large of a domain is required for low uncertainty?



Should run simulations on large domain – (80 μm)^3

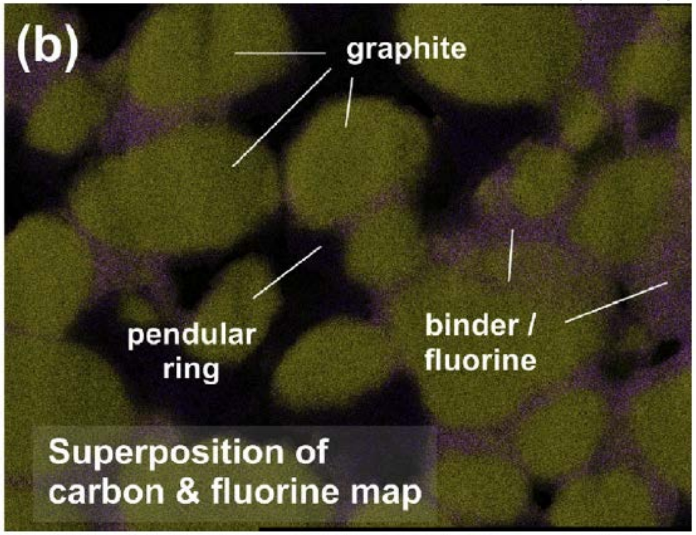
Technical: Binder Representation

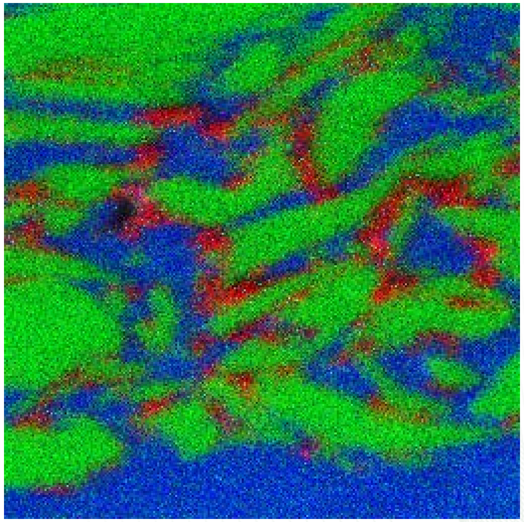
- Resolving the location of active binder (PVDF + CB) is much more difficult than active/non-active image segmentation.
- Binder is often neglected, assuming non-active void space is entirely electrolyte.
- Limited imaging results can hint at binder location:

CB/PVDF wt %	NMC/AB Volume Ratio
2-2 wt%	9.62
3-3 wt%	6.23
4-4 wt%	4.61
5-5 wt%	3.61

CB = carbon black
AB = active binder = PVDF + CB

Jaiser et al. (2017)





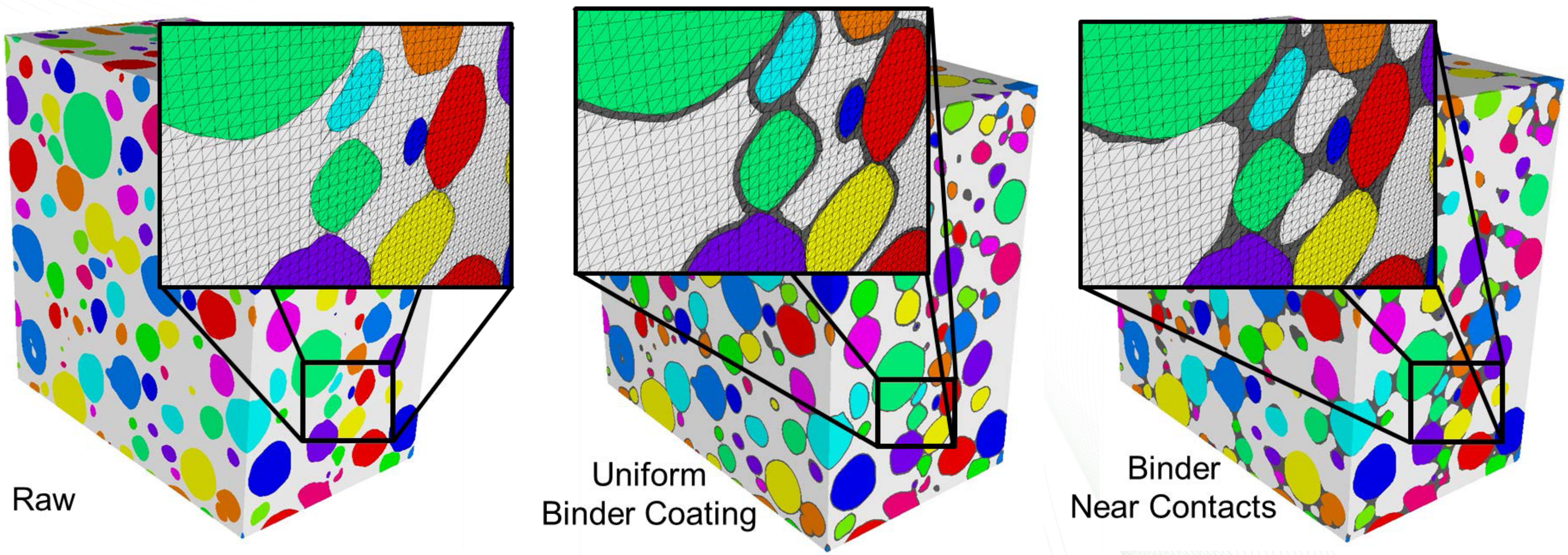
TOF-SIMS for graphite anode

Red: PVDF
Green: Carbon
Blue: Epoxy (Voids)

How are properties affected by inclusion of binder?

Technical: Binder Representation – Approach

- No high-quality images of NMC with binder resolved
- How can we manufacture a microstructure to include binder?

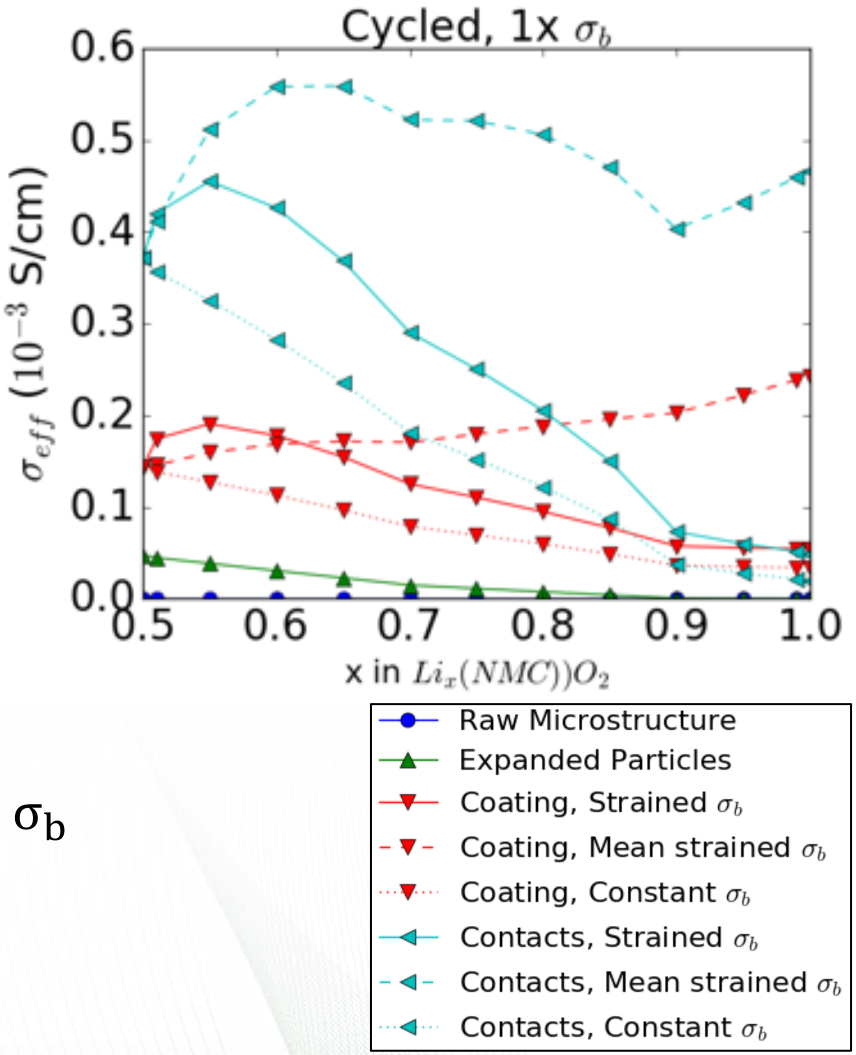


Trembacki (submitted)

Placing binder near contacts is most physical looking

Technical: Binder Representation – Behavior

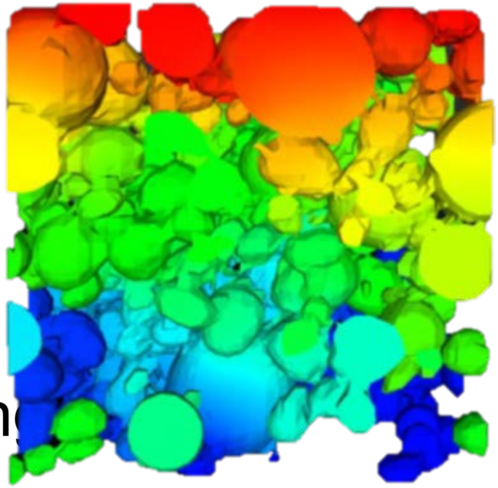
- Expanded particles: low σ_{eff}
- Competing effects as Li increases:
  - Reduced σ_{NMC}
  - Increased σ_b (particle swelling)
- σ_{eff} is relatively insensitive to lithiation
- Constant σ_b: up to 2x σ_{eff} decrease
- Mean strained σ_b overpredicts σ_{eff}
- Strain-dependence and localization of σ_b have significant effects on σ_{eff}



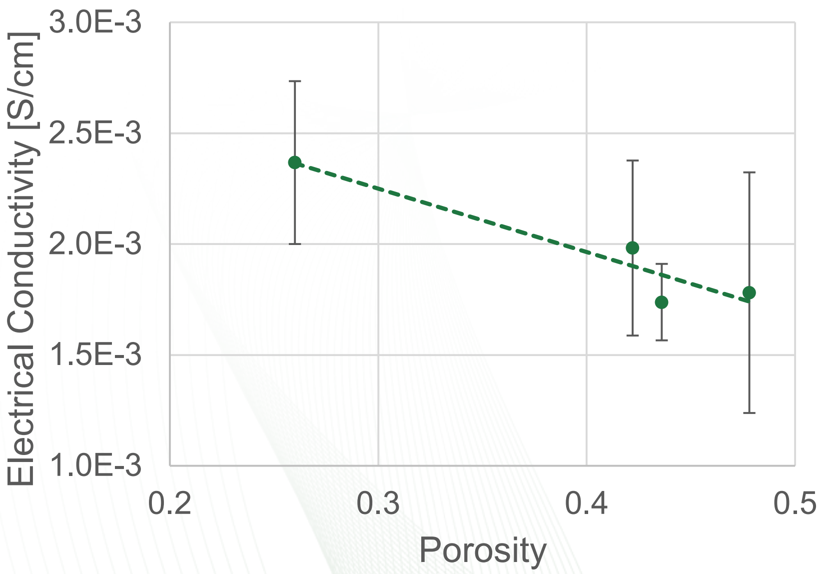
Trembacki (submitted), Grillet (2016)

Nature of binder placement significantly affects performance

Technical: Crush Response



- When an electrode is crushed (i.e. in a car crash), the electrode can locally compact (reduce porosity)
- Process may have similar effect as calendaring
- Microstructure simulation at 4 porosities
- Electrical conductivity increases with increasing pressure, decreasing porosity
- Feed these results into battery-scale simulation
- With ORNL (I.4)



Inform battery-scale crush simulation with microstructure

Responses to Previous Year Reviewers' Comments

- Highlight importance of binder modulus; source of data
  - Agree that mechanical degradation of active binder is critical performance parameter. Current treatment is simple (elastic) but currently expanding to consider nonlinear effects (creep) and aging. Primary source of mechanical data is Grillet (2016), although other publications recently appearing in then literature.
- Minimum RVE size for tomography/microstructure simulations; statistical nature of failure
  - Minimum RVE is crucial, as is the resolution of particle shape. This is why a CT approach is taken, rather than FIB/SEM (which has small field of view). Previous studies of simulation domain size variability speak to RVE requirements and number of samples required to obtain statistically significant results.

Any proposed future work is subject to change based on funding levels

Collaboration and Coordination with Other Institutions

Organization	Type	Relat.	VT?	Extent
Oak Ridge National Laboratory	Natl. Lab	Prime	Y	Upscaling to battery sims, experiments
Lawrence Berkeley National Laboratory	Natl. Lab	Peer Sub	Y	Tomography, microscale simulations, experiments
Argonne National Laboratory	Natl. Lab	Peer Sub	Y	Tomography
National Renewable Energy Laboratory	Natl. Lab	CAEBAT	Y	General collaboration, sharing of results and ideas
Texas A&M University	Acad.	CAEBAT	Y	Microstructure simulation collaboration
Duracell	Indust.	CRADA	N	Shared microstructure / electrochemistry development

Broad collaboration improves our work

Remaining Challenges and Barriers

- Efficiency / robustness of microscale electrochemistry
  - Anisotropic mesh elements lead to poor convergence
  - Mesh requirements lead to long-running simulations
- High-quality, controlled microstructure reconstructions at controlled conditions that resolve active binder phase
  - Active binder apparently impossible to detect with X-rays
- Availability / quality of microscale validation data
  - Significant uncertainty in input parameters boosts importance of validating results against experimental data
- Quantitative properties of active binder phase
  - Conductivity, swelling, modulus

Any proposed future work is subject to change based on funding levels

We address these risks in our future work

Proposed Future Research

- Complete efficient and robust microscale electrochemistry
  - Improve mesh quality through changes to CDFEM algorithm
  - Stabilized boundary conditions to improve speed, robustness
- Coordinate with LBNL/ANL to quality, consistent microstructures
- Develop and test manufactured active binder representation
- Coordinate with ORNL/LBNL to measure electrode-scale properties for model validation
- Implement nonlinear models of active binder mechanics
- Collaborate with ORNL to implement microstructure simulations and results into battery-scale simulations

Any proposed future work is subject to change based on funding levels

Future work tailored to address key risks, milestones

Summary

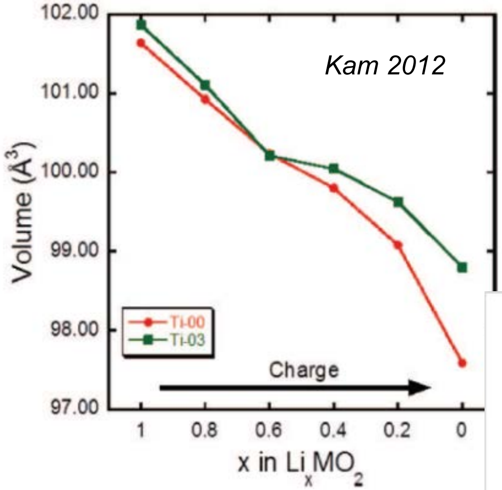
- **Objective:** Create high-fidelity microstructure simulations of Li-ion battery electrodes to inform battery-scale simulations of operation and abuse
- **Results:**
  - Demonstrated microstructure simulations of NMC cathode, including a manufactured representation of active binder phase
  - Verified numerical approach and quantified required mesh resolution, domain size for statistically significant results
- **Results (cont.):**
  - Used microstructure simulations to create conductivity vs. porosity relationships for use in crush abuse simulations
- **Future work:**
  - Perform microscale simulations of coupled electrochemical-mechanical performance of NMC
  - Predict electrode swelling during operation
  - Integrate microstructure simulation capability into battery-scale simulation framework

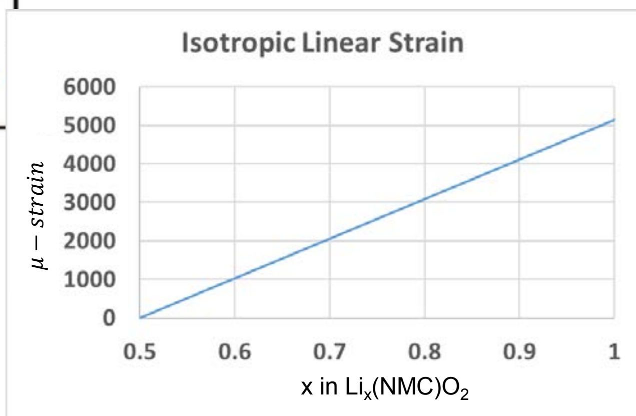
Any proposed future work is subject to change based on funding levels

Technical Back-Up Slides

Lithiation-dependent material properties

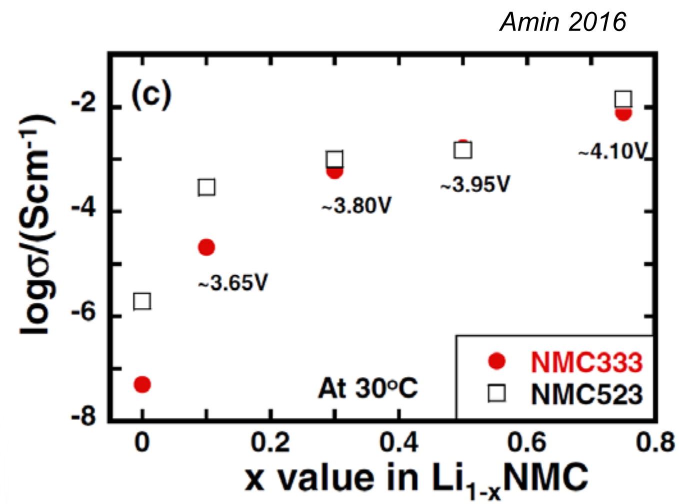
Isotropic swelling





- Linear fit to data to get strain vs. Li_x
- Assume stress-free at x=0.5
- ~1.55% volume change

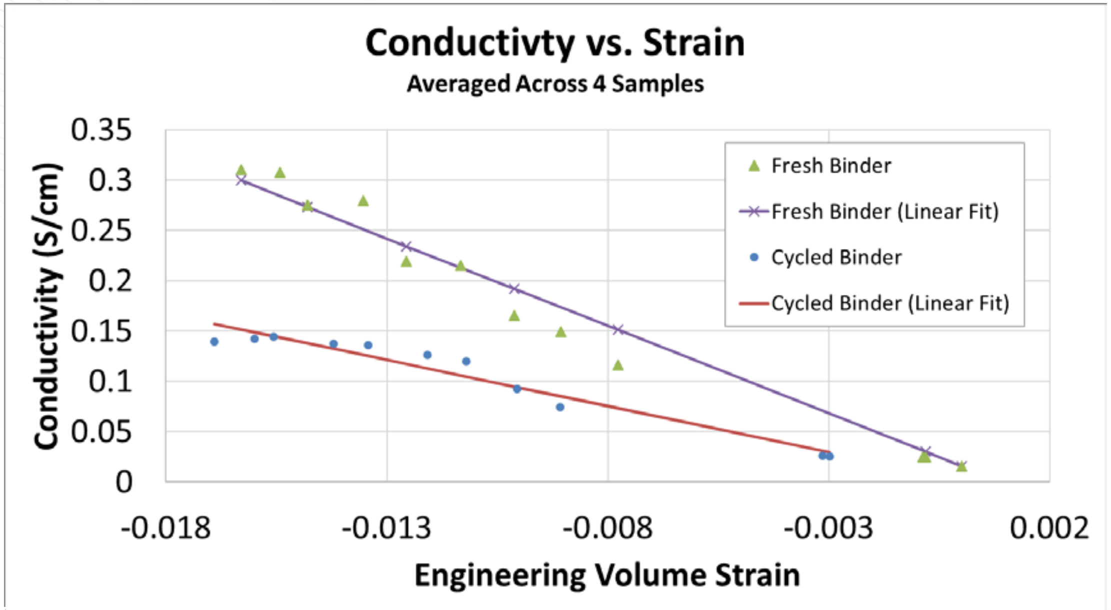
σ_{NMC}



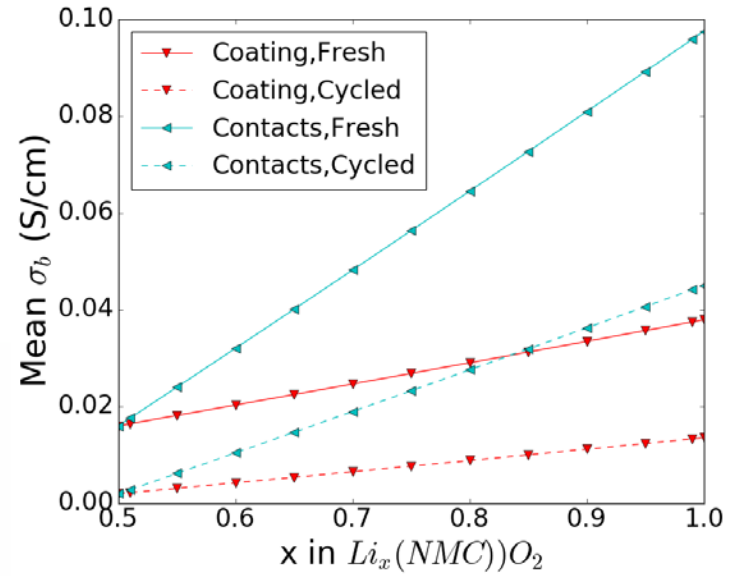
- Conductivity significantly decreases with NMC lithiation (4 orders of magnitude)

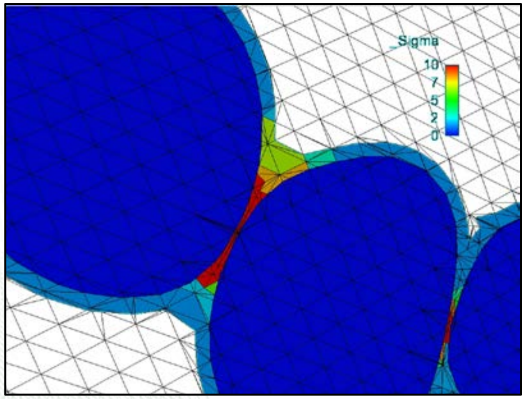
Lithiation-dependent material properties

Strain-dependent σ_{binder}



Grillet 2016





- Fit active binder conductivity to experimental data, capped at 5 S/cm
- As particles swell, binder is compressed, increasing conductivity
- Conductivity magnitudes lower than literature